Preparation of Zeolites Supported on Optical Microfibers

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Samples of zeolites supported on optical microfibers were prepared with tetraethyl orthosilicate (TEOS) as a binding agent using sol−gel methods. A slower rate of TEOS hydrolysis in the sol−gel relative to the rate of silanol condensation was observed to be crucial for successful support of the zeolite particles on the optical fibers. The amount of water and the pH of the reaction gel were varied to control and optimize the rates of hydrolysis and condensation. Scanning electron microscopy (SEM), Brunauer−Emmett−Teller (BET) surface area measurements, and thermogravimetric analysis (TGA) were used to characterize the zeolite particles on the optical microfibers. The zeolite adhesion obtained was robust as the particles sustained spinning at 2000 Hz and suspension in flowing water for 12 h. The zeolite-supported optical fibers provide an improved catalyst system for the introduction of light into zeolite pores.

Introduction

For many practical applications of photocatalysis, the immobilization of the photocatalyst in a fixed-bed reactor configuration is desirable.[1] In a conventional fixed-bed reactor, the photocatalyst is supported on the wall of the reactor or on a matrix such as the lamp casing, glass beads, glass plates, or a fiberglass mesh to name a few. However, these configurations present several drawbacks including low light utilization due to adsorption and scattering effects by the photocatalyst or its support. Additionally, mass-transport limitations are a concern for potential systems. Ollis and Maringeli proposed a novel approach to solving these problems that employed optical fibers as a means of light transmission and distribution to the supported photocatalysts.[2,3] Hoffmann et al. developed a photochemical reactor system that used an optical fiber cable to transport light to TiO_2 particles chemically anchored onto the quartz fibers.[1,4] Irradiation of the TiO_2 particles occurred by refraction of light from the fiber.[4] With this system a 4-fold increase in the quantum efficiency was achieved for the degradation of 4-chlorophenol as compared to a TiO_2 slurry reactor operated under similar conditions.[1] In our laboratory, we have found that the use of TiO_2-coated optical microfibers can improve the photocatalytic efficiency for the degradation of trichloroethylene and ethanol.[5,6]

Zeolite-induced photocatalysis has important potential application in such areas as pollution control, selective oxidation reactions for the production of fine chemicals, and chiral synthesis of pharmaceutical compounds. Anpo et al. have shown that the photoefficiency of titanium dioxide catalysts can be improved by dispersing isolated TiO_2 clusters in zeolite channels.[7,8] Langford et al. reported that titania supported on ZSM-5 zeolite resulted in high photoactivity (especially at low Ti loadings) for the photodegradation of acetophenone and 4-chlorophenol in aqueous solution.[9] The same group recently reported that TiO_2 supported on MCM-41 is also a promising photocatalyst.[10] Frei et al. reported a simple method for the partial oxidation of small alkenes, alkanes, and alkyl-substituted benzenes by oxygen with unprecedented selectivity.[11−14] Chiral induction of chemical reactions is another area of interest to chemists. Ramamurthy et al. have modified zeolites with chiral inductors to achieve enantioselectivities of photocatalytic products as high as 90%.[15] Scale-up of these photocatalytic applications ultimately requires immobilization of modified zeolite particles on transparent substrates.

Zeolite adhesion on supports can be accomplished by direct synthesis of zeolites on a support or by applying prepared zeolites to the support. Most of the currently

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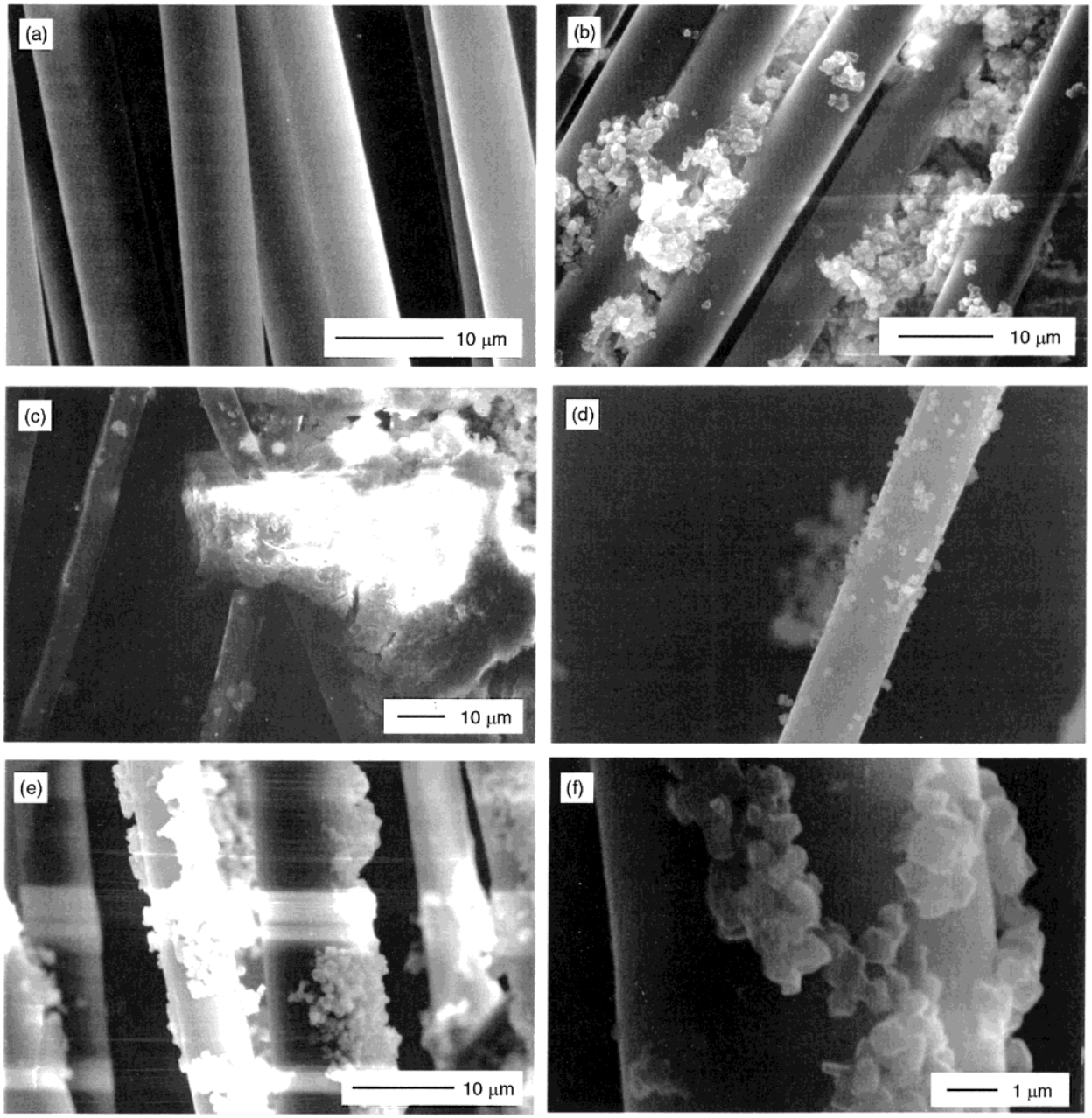

Figure 1. SEM images of (a) quartz optical microfibers after the cladding was removed and BaY zeolites attached to quartz optical microfibers prepared (b) by wet impregnation from an ethanol solution, (c) at autogenous pressure from a TEOS solution, (d) using the sol−gel method from a TEOS solution with a single application of zeolites, and (e) using the sol−gel method from a TEOS solution with three applications of zeolites. (f) Magnified SEM image of a single application of zeolites on quartz optical microfibers using the sol−gel method as in d. Some SEM images do not have bar scales because they were not added at the time of the scan, but the scale can be approximated from the diameter of the fibers (7−7.5 μm).

reported work is carried out by the direct synthesis method.[16,17] There are very few examples of three-dimensional objects coated with films of presynthesized zeolites. Among these is an approach reported by Bein et al. that uses a silane coupling agent to coat gold electrodes or quartz crystals with zeolite−silica thin films.[18,19] Yoon et al.[20] reported the use of ionic and covalent linkers to attach zeolite crystals to various substrates. However, it is not clear from these publications whether such techniques could be used to assemble materials for practical applications that require high-temperature activation. Recently, we demonstrated the increased photoefficiency for the selective oxidation reaction of chlorinated hydrocarbons with zeolites supported on optical microfibers.[21] In a more recent communication, we demonstrated that zeolite-coated quartz fibers prepared by this technique used to carry out

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asymmetrical photoreactions and to detect polyaromatic compounds.[22] In this paper, we report a detailed study on the preparation of supported zeolite particles on optical microfibers and the optimization of parameters to achieve improved coverage and binding strength of the zeolite particles on the optical fibers.

Experimental Section

Sample Preparation. Three methods for bonding zeolite particles to optical microfibers were investigated: the wet impregnation method, the use of silica sol at autogenous pressure, and the sol−gel method using dip-coating. Quartz optical microfibers (9 μm in diameter) were obtained from Quartz Products Company (Louisville, KY). Before application of the zeolites, the polyimide cladding of the quartz fibers was removed by calcination at 753 K for 8 h in the presence of flowing oxygen, followed by treatment with piranha solution (7:3 concentrated H_2SO_4/30% H_2O_2) at 363 K for 1 h. The fibers were then rinsed with distilled water and dried. The diameter of the microfibers after the cladding was removed is approximately 7−7.5 μm, as determined from the SEM image shown in Figure 1a. Cut and segregated microfibers (1.5 cm in length) were used for the experiments. Zeolite BaY was prepared from NaY zeolite obtained from Zeolyst International by ion exchange with a 0.5 N $BaCl_2$ solution. The optical fiber supports were prepared with BaY zeolite, but other zeolites can be used.

The wet impregnation method employed a dispersion of 0.50 g of BaY powder in 15 mL of ethanol. This mixture was stirred while 0.40 g of the bare optical fibers was added. The mixture was evaporated to dryness to facilitate condensation of the zeolite particles to the optical fibers. The fibers were then calcined in air at 753 K for 8 h.

In the second approach, a silica sol was prepared by adding 5 mL of tetraethyl orthosilicate (TEOS) to 5 mL of ethanol. A small amount of acid (approximately 0.5 mL of 0.04 M HCl) was added to the silica sol as a silicate oligomerization catalyst. A mixture was prepared by combining in sequence 5 mL of ethanol, 0.50 g of BaY zeolite, 0.40 g of bare optical fibers, and 1.0 mL of silica sol. The mixture was transferred to an autoclave and maintained at 343 K under autogenous pressure for 12 h. The autoclave was then cooled to room temperature. The fibers were filtered, washed with ethanol, dried at 333 K in a vacuum oven, and calcined at 753 K in air for 8 h.

The last procedure investigated for bonding zeolite particles to the optical fibers was the sol−gel process using a TEOS solution. In a typical procedure, silica sol was prepared by adding 0.713 g of TEOS to 4.0 g of ethanol under stirring. Hydrochloric acid (3 μmol) was added to the silica sol as the silicate oligomerization catalyst. The rate of hydrolysis of TEOS was controlled by adding appropriate amounts of water to vary the H_2O/TEOS mole ratio between 0.0010 (0.0010 g H_2O) and 16 (0.931 g H_2O). Bare optical fibers (0.40 g) were added to the silica sol, and the mixture was allowed to settle for 12 h. The mixture of silica sol and optical microfibers was heated under constant stirring at 343 K until the ethanol evaporated to dryness (approximately 1 h). The silicate-coated optical fibers were then dip-coated in 0.50 g of BaY suspended in 15 mL of ethanol. The mixture was stirred overnight and dried at 343 K in a vacuum oven for 0.5 h. The procedure of dip-coating the optical microfibers was repeated three times to improve the zeolite coverage. More than three dip-coating cycles resulted in the formation of agglomerates of zeolite particles on the microfibers. Annealing of the zeolite particles to the optical fibers was achieved by calcination of the zeolite/silicate optical fibers at 753 K in air for 12 h.

The effect of pH on zeolite adhesion was studied. The pH of the silica sol from the sol−gel method using dip-coating was varied from 1.7 to 10.4 by adding HCl or NH_4OH (28% NH_3) to the silica−sol solution. SEM images of the coated fibers were used to determine the optimum pH.

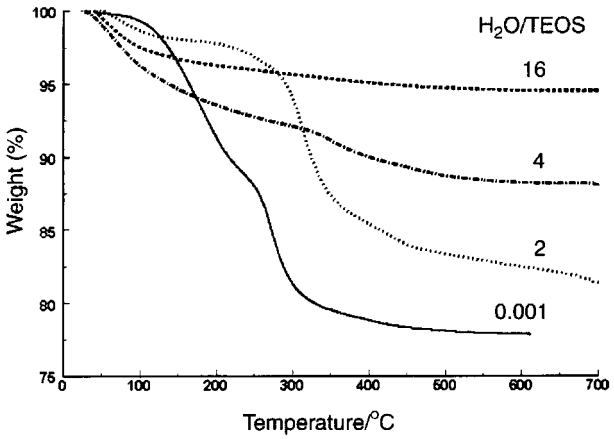

Figure 2. Thermograms of the silicate optical microfibers prepared from the silica sol with various H_2O/TEOS mole ratios.

Characterization. The physical and chemical transformations during the conversion of the silica sol to a gel on the optical fibers was monitored by thermogravimetric analysis (TGA) at a heating rate of 10 °C min^{-1} in the presence of air. SEM was used to investigate the nature and extent of the zeolite coverage. The BET surface area of the zeolites supported on the optical fibers under optimized reaction conditions (the sol−gel method with a H_2O/TEOS mole ratio of 0.0010 and three dip-coatings) was 124 m^2/g, and the surface area of the cleaned optical microfibers was negligible. Weight differences and control studies suggest that the approximate contribution of the zeolite particles to the zeolite optical fiber samples is approximately 34%. The binding strength was evaluated by spinning the fibers at 2000 Hz in a solid-state nuclear magnetic resonance (NMR) probe and by subjecting them to flowing water for 12 h. SEM images of the fiber-supported zeolites were used to determine the condition of the zeolites after these tests. The zeolite fibers were studied in our laboratory as photocatalysts for the degradation of chlorocarbons using solid-state NMR spectroscopy.[21]

Results and Discussion

The three methods explored for bonding zeolite particles to optical microfibers are shown in the SEM images in Figure 1b−f, along with an SEM image of the bare quartz optical microfibers after the polyimide cladding had been removed (Figure 1a). As seen in Figure 1b, the coverage of the zeolite prepared by the wet impregnation method is nonuniform. Moreover, when the sample was spun at 2000 Hz, all of the particles separated from the optical fiber surface. Figure 1c shows the result of adhering the zeolite particles to the fibers using TEOS as the binding agent at 343 K and autogenous pressure. It was observed that, instead of the zeolites bonding to the surface of the optical fibers, amorphous silica precipitated from the hydrolyzed TEOS. The results of adhering zeolites to the fibers using the sol−gel method with dip-coating are shown in Figure 1d. The zeolite coverage is more uniform and highly stable. Multiple applications of the zeolite particles were prepared to increase the extent of the coverage on the optical fibers. The SEM micrograph of the sample prepared with three zeolite applications is shown in Figure 1e, and a magnified image of a single application of zeolites is shown in Figure 1f.

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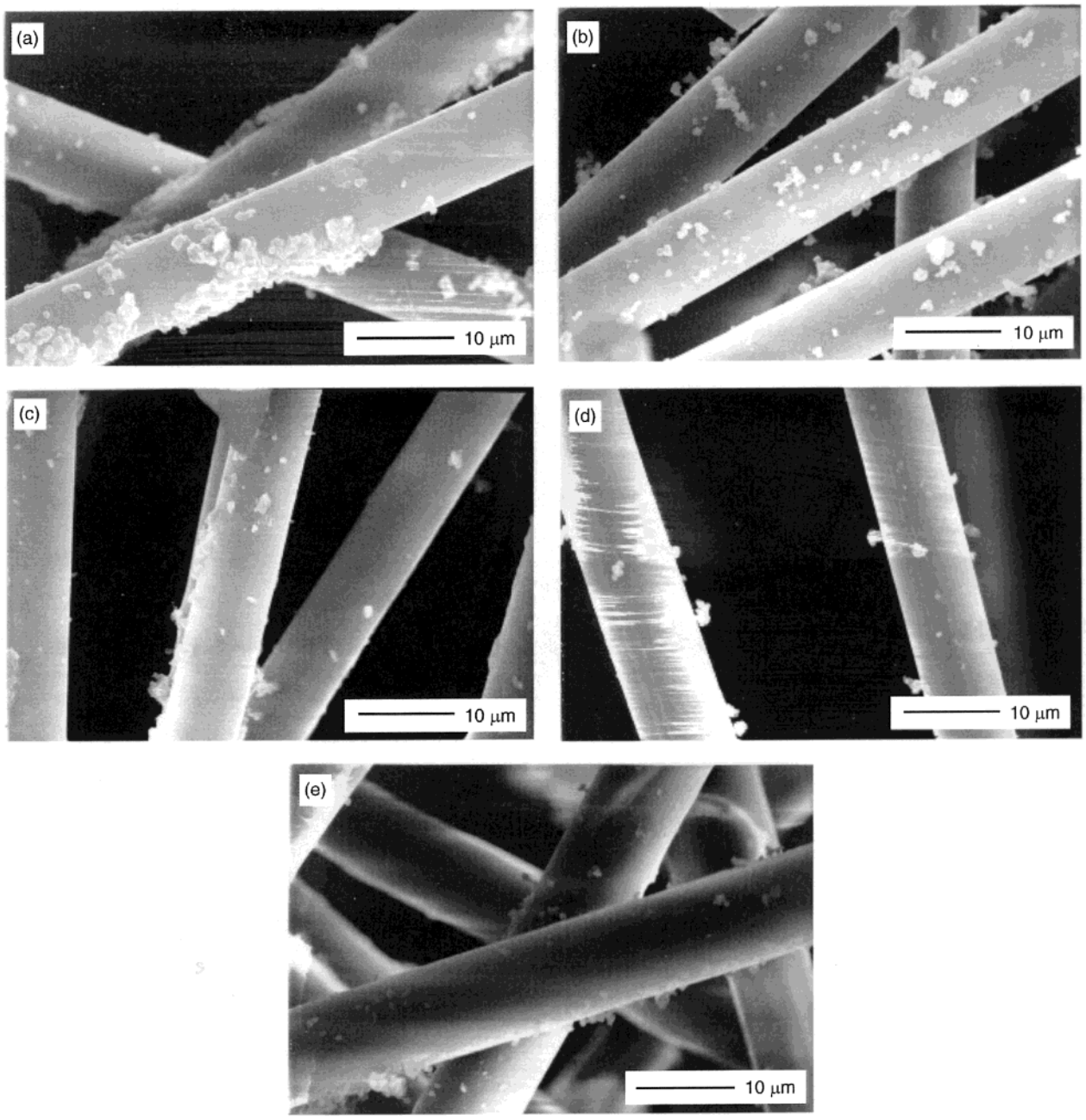

Figure 3. SEM images of the zeolite/silicate optical microfibers prepared from the sol−gel method with the silica sol at a pH of 1.4 and H_2O/TEOS mole ratios of (a) 0.001, (b) 2.0, (c) 4.0, and (d) 16.0 and (e) similarly prepared using a H_2O/TEOS mole ratio of 0.001 at pH 10.4.

An important objective of this study was to optimize the extent and binding strength of the zeolite particles on the optical microfibers. It was found that these parameters could be met by controlling the rate of hydrolysis of TEOS. It is known that the chemical transformation of the silicate gel began with hydrolysis of TEOS to form silanols. Condensation of the silanol groups occurred to form silicate polymers, which linked together to form the gel.[23] The relative rates of hydrolysis and condensation depend on three factors: the concentration of water, the concentration of TEOS, and the pH of the sol−gel.[23] The effects of these parameters on the zeolite coverage were studied by varying the H_2O/TEOS mole ratio and the pH of the gel.

Effect of H_2O/TEOS Mole Ratio. Brinker et al. have shown that, when the water concentration in the gel is increased, decreases in the bulk density and specific surface area of the gel are observed.[23] The gel behavior prior to the zeolite attachment was monitored by TGA, and the results are shown in Figure 2. The thermograms can be divided into three distinct regions. Region I (T < 125 °C) corresponds to desorption of physically adsorbed water and solvent, region II (125−250 °C) corresponds to carbonization of residual alkoxy groups, and region III (250−400 °C) is typical of carbon combustion. According to Brinker et al., the weight loss in region III scales with the EtO/Si ratio of hydrolyzed

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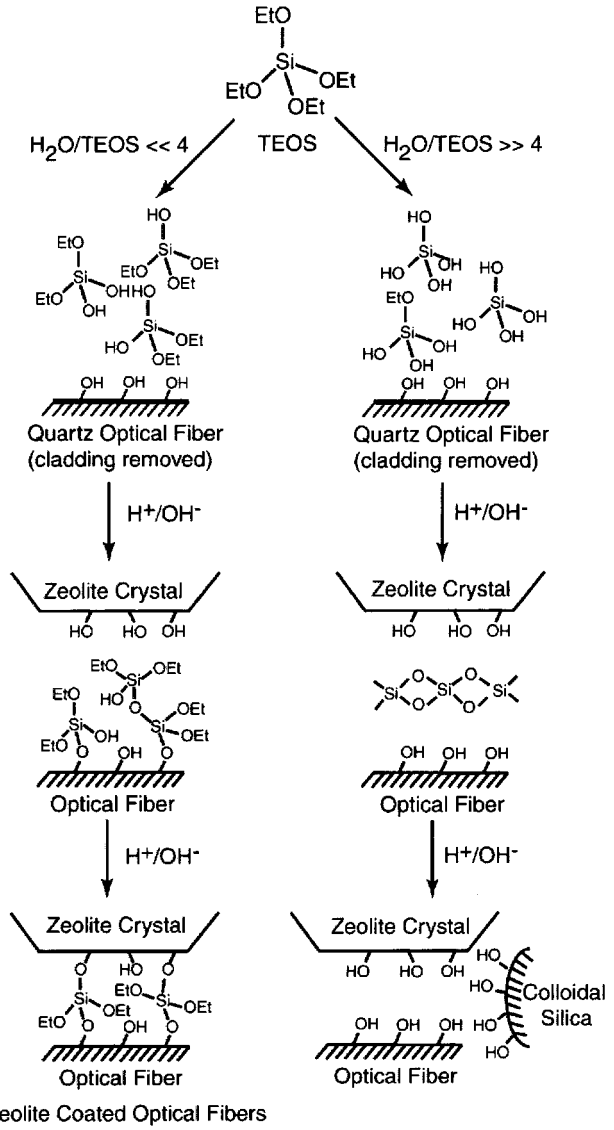

Figure 4. Schematic representation of the proposed reaction mechanism for the preparation of zeolite optical fibers at various water concentrations in the gel.

TEOS.[23] At a low H_2O/TEOS mole ratio, the weight losses in regions II and III are much higher, while the corresponding loss in region I is lower. At higher H_2O/TEOS mole ratios, these trends are reversed. The results indicate that the extent of hydrolysis of the ethoxide groups is controlled by the amount of water in the silica sol.

SEM micrographs of the zeolites supported on the optical fibers prepared using silica sols with varying H_2O/TEOS mole ratios are presented in Figure 3. As can be seen in the micrographs, the extent of zeolite coverage decreases with increasing H_2O/TEOS mole ratio. The results indicate that the presence of ethoxide groups in the silica sol is necessary for the attachment of the zeolite particles to the optical fibers.

A possible reaction mechanism for the formation of the zeolite bonding in the silica sol is presented in Figure 4. As shown in the figure, with excess water (H_2O/TEOS > 4) the hydrolysis of the ethoxide groups of TEOS is complete, and monosilicic acid forms. In the presence of base or acid, the monosilicic acid polymerizes to form highly condensed, cross-linked SiO_2.[23] The result

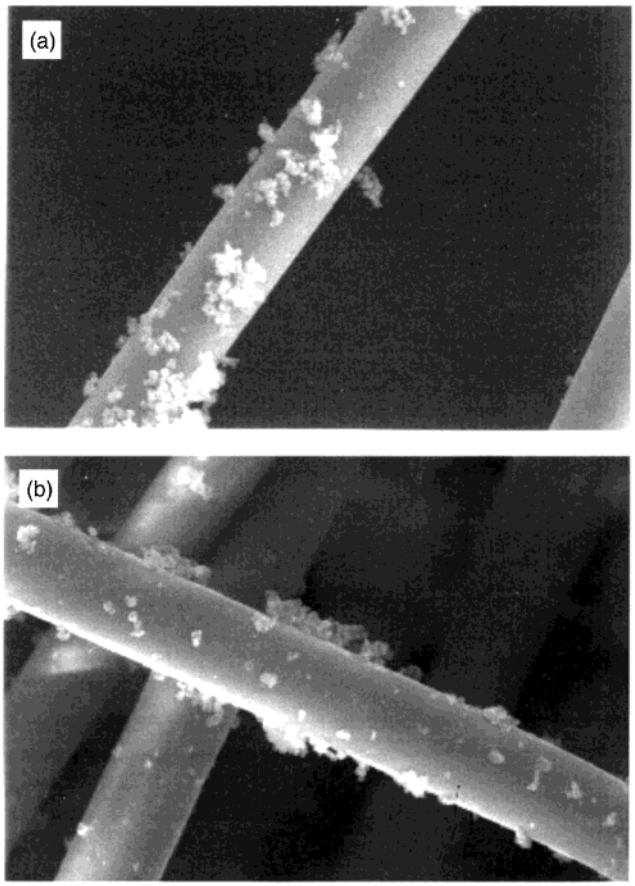

Figure 5. SEM images of the zeolite optical microfiber sample (presented in Figure 3a) after (a) spinning at 2000 Hz for 12 h and (b) being subjected to flowing water for 12 h.

is a silica gel with a high water concentration does not act as a good binding agent for the zeolite particles because it precipitates as highly cross-linked silica gel.

On the contrary, at low concentrations of water in the silica sol (H_2O/TEOS < 4), the rate of condensation of the silanols is greater than the rate of their formation by hydrolysis from TEOS. The proposed mechanism of the acid-catalyzed hydrolysis of TEOS involves coordination of an acid and a water molecule with TEOS, followed by electrophilic attack of the alkoxide oxygen.[23,24] Hydrolysis under these conditions is sensitive to steric effects, as the water substitutes from one side of the TEOS molecule while the acid stabilizes the exiting ethoxide group. Because the TEOS molecules condense while they are only partially hydrolyzed, further hydrolysis and condensation is slowed, preventing the mass precipitation of SiO_2. Thus, the condensation reactions between the zeolite particles, the silica gel, and the quartz fibers are more favorable and result in bonding of the zeolite particles to the fibers. Silanol groups of the coated silica gel on the optical fibers become anchoring centers for further zeolite attachments.

Effect of pH. As the pH of the gel was varied from 1.7 to 10.4 by the addition of HCl or NH_4OH, the synthesis procedure resulted in an inefficient coverage of the zeolite particles on the optical fibers (see micrograph in Figure 3e). The result can be explained by the fact that, in the basic medium, hydrolysis of TEOS proceeded much more rapidly than condensation of the

silanol groups resulting in the formation of silicate polymers.[23] Complete hydrolysis of the alkoxides resulted in unproductive annealing of the zeolite particles to the optical fibers.

Binding Strength of the Zeolite Particles. Applications of zeolites to photocatalysis, environmental catalysis, chiral and other chemical synthesis, sensors, and electronic applications requires strong binding of the zeolite particles to the substrate to sustain operation under conditions such as strong currents of air or water. In our laboratory, we have studied supported solid photocatalysts such as TiO_2, V_2O_5, SnO_2, WO_3, mixed-metal oxides, and zeolites using solid-state NMR spectroscopy.[25] For solid-state NMR analysis, the particles on the fibers must withstand the conditions of magic angle spinning on the order of several kilohertz. To study the binding strength of the zeolite particles, the fiber-supported zeolites were subjected to spinning at 2000 Hz for 12 h and to flowing water for 12 h. The SEM micrographs of the fibers after these tests are shown in Figure 5. As can be seen in these micrographs, no noticeable change in the zeolite coverage was observed after these tests. These results indicate that the zeolite crystals are bound strongly enough to sustain the severe conditions required for a variety of different applications. The covalent bonds between the native oxide surface of the optical fibers, the silica binder, and the zeolite particles make the attachments robust.

Conclusions

Zeolite particles were attached to optical microfibers with the sol−gel method using dip-coating. The wet impregnation method and the sol−gel method at autogenous pressure resulted in little or no adhesion of zeolite particles. The sol−gel method from a TEOS solution is effective in adhering zeolite particles to the fibers when hydrolysis of the alkoxide groups is limited during gel formation. The hydrolysis reaction can be mitigated by controlling the amount of H_2O added to the gel and the pH of the gel. The best conditions found in this study for the sol−gel method with dip-coating are a pH of 1.7, a H_2O/TEOS mole ratio of 0.0010, and multiple applications. The zeolite coverage obtained in this way can tolerate extreme operating conditions, such as spinning of the sample at 2000 Hz and flowing under a stream of water, which are required for technically advanced photocatalysis or other chemical applications.

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